

## Articles

# Determination of Mercury in Coal by Isotope Dilution Cold-Vapor Generation Inductively Coupled Plasma Mass Spectrometry

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**A method based on isotope dilution cold-vapor inductively coupled plasma mass spectrometry (ID-CV-ICPMS) has been developed for high-accuracy determinations of mercury in bituminous and sub-bituminous coals. A closed-system digestion process employing a Carius tube is used to completely oxidize the coal matrix and chemically equilibrate the mercury in the sample with a  $^{201}\text{Hg}$  isotopic spike. The digestates are diluted with high-purity quartz-distilled water, and the mercury is released as a vapor by reduction with tin(II) chloride. Measurements of  $^{201}\text{Hg}/^{202}\text{Hg}$  isotope ratios are made using a quadrupole ICPMS system in time-resolved analysis mode. The new method has some significant advantages over existing methods. The instrument detection limit is less than 1 pg/mL. The average blank ( $n = 17$ ) is 30 pg, which is roughly 1 order of magnitude lower than the equivalent microwave digestion procedure. The detection limit in coal is blank limited and is  $\sim 40$  pg/g. Memory effects are very low. The relative reproducibility of the analytical measurements is  $\sim 0.5\%$  for mercury concentrations in the range 10–150 ng/g. The method has been used to measure mercury concentrations in six coal reference materials, SRM 1632b (77.4 ng/g), SRM 1632c (94.3 ng/g), BCR 40 (433.2 ng/g), BCR 180 (125.0 ng/g), BCR 181 (135.8 ng/g), and SARM 20 (252.6 ng/g), as well as a coal fly ash, SRM 1633b (143.1 ng/g). The method is equally applicable to other types of fossil fuels including both crude and refined oils.**

Interest in mercury cycling within the environment has risen dramatically in recent years as a result of high levels of methylmercury appearing in the aquatic food web, most significantly

in fish. More than two-thirds of the contiguous states within the United States now have fish advisories for selected lakes, rivers, and coastal waters, limiting the consumption of fish of noncommercial origin. Ingestion of methylmercury can damage the central nervous system and disrupt the endocrine system.<sup>1</sup> Although mercury enters the aquatic environment from a number of domestic sources, such as paper mills, solid waste incineration, mining, and chlor-alkali production, the burning of fossil fuels for electric power generation is generally considered to be the largest single anthropogenic contributor. Approximately 93% of U.S. coal consumption is used to generate electricity, and the U.S. EPA has estimated<sup>2</sup> that  $\sim 4.7 \times 10^7$  g (52 U.S. short tons) of mercury is emitted annually as a result of this process, which represents approximately one-third of total estimated anthropogenic emissions. Although electric power plants emit relatively little methylmercury, bacterial conversion of deposited inorganic mercury into methylmercury readily occurs within water bodies. Bioaccumulation factors of several million in fish mean that even modest amounts of mercury emissions may result in a significant toxicological hazard to at-risk population groups, most notably developing fetuses and young children. To address this issue, the U.S. EPA, in accordance with the 1990 Clean Air Act Amendments, issued a report<sup>2</sup> detailing a study of atmospheric mercury emission sources and their implications for human health and at the end of 2000 decided to regulate mercury emissions from coal-fired utilities.

To assess and monitor the contribution of mercury from coal, there is a need to measure accurately the mercury content in this complex and difficult matrix and to have a reliable traceability

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(2) U.S. EPA *Mercury Study Report to Congress*; Office of Air Quality Planning and Standards and Office of Research and Development: Washington DC, 1997.

basis with which to compare these measurements. Several analytical techniques have been used for the determination of mercury in coal. The most commonly used technique is cold-vapor atomic absorption spectrometry (CVAAS).<sup>3–9</sup> Other techniques including atomic fluorescence spectrometry (AFS),<sup>10–13</sup> radiochemical neutron activation analysis (RNAA),<sup>14–18</sup> and inductively coupled plasma mass spectrometry (ICPMS)<sup>6,19</sup> have also been used. The removal of mercury from the coal matrix by mild pyrolysis combined with a variety of detection methods has also been employed.<sup>10,14,15,20–23</sup> Evans et al.<sup>24</sup> used pyrolysis in an oxygen stream at 1200 °C to remove mercury from several coal and fly ash materials prior to measurement of high-precision isotope ratios using four different multicollector ICPMS instruments. Owing to the low levels of mercury in the materials, the mercury was preconcentrated on gold and the measurements were made on transient signals.

Although CVAAS is very sensitive and easily automated, it is susceptible to nonspecific spectral interferences from residual unoxidized organic bonds and free chlorine. Given the complexity of the coal matrix and that the levels of mercury in coal are generally quite low, this is not an easy determination to make accurately. Similarly, neutron activation analysis, using the activated <sup>203</sup>Hg isotope, is subject to a significant spectral interference from selenium, which is also present in coal. The severity of this interference necessitates a radiochemical separation of the selenium and mercury, the use of a peak-ratio spectral interference correction process, or both. This limits the attainable accuracy and detection limit. A recent exhaustive review of the merits and limitations of all techniques for the trace determination of mercury has been provided by Winefordner and co-workers.<sup>25</sup> Clearly, the

development of a method based on isotope dilution coupled with ICPMS measurement should be relatively immune to many, if not all, of these analytical limitations. Yoshinaga and Morita<sup>26</sup> used isotope dilution with nebulization sample introduction to measure mercury in biological and environmental samples. The use of electrothermal vaporization (ETV) combined with isotope dilution ICPMS has been reported by several groups.<sup>27–29</sup> Hintelmann and Evans<sup>30</sup> used gas chromatography (GC) and isotope dilution ICPMS for application to environmental tracer studies of methylmercury. Snell and co-workers<sup>31</sup> also used this approach to investigate mercury species in natural gas condensates.

Several interlaboratory studies have been conducted to assess the status of mercury determinations in coal. Lengyel et al.<sup>32</sup> of CONSOL Corp. (Pennsylvania) conducted an interlaboratory and intralaboratory variability study in 1996, supplying splits of two American seam coals and NIST 1632b, Trace Elements in Coal, to 11 participating laboratories in two phases over a one-year period. The study indicated that even state-of-the-art procedures resulted in approximately 50% interlaboratory variability and 27% intralaboratory variability. The authors concluded that the accuracy of mercury in coal measurements needed to be improved. Another more recent and comprehensive round-robin study<sup>33</sup> was sponsored by the Electric Power Research Institute (EPRI), Palo Alto, CA, to evaluate the adequacy of test methods for mercury (and chlorine) in coal. The study was conducted in two phases and involved the participation of 40 commercial, government and power producer facilities, employing almost exclusively CVAAS measurement in concert with several ASTM preparation methods. Interlaboratory variability across all methods ranged from 10% to 45% relative standard deviation depending on the level of mercury in the coal, with lower levels producing notably poorer performance.

Both of these intercomparison studies were hindered to some extent by the lack of certified reference materials, as was noted in the CONSOL study.<sup>32</sup> A high-accuracy method based on isotope dilution cold-vapor generation inductively coupled plasma mass spectrometry (ID-CV-ICPMS) has therefore been developed to address this issue. The selectivity and sensitivity of both cold-vapor generation ICPMS coupled with the inherent accuracy of isotope dilution results in a significant analytical advantage.<sup>34,35</sup> The method employs a high-pressure closed-system digestion using a Carius tube. This approach simultaneously addresses the most significant issues limiting accuracy in measurement, namely, analyte loss, blank control, total chemical equilibration, and complete destruction of the chemical matrix. The method has been used to measure mercury in NIST SRM 1632b (Trace

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Elements in Coal), 1632c (Trace Elements in Coal), and 1633b (Coal Fly Ash). Several certified reference materials (CRMs) from the Community Bureau of Reference (BCR), Belgium, and from the South African Bureau of Standards (SABS), South Africa, were also measured.

## EXPERIMENTAL SECTION

**Reagents.** High-purity nitric acid was prepared at NIST using a sub-boiling distillation apparatus and stored in double-bagged Teflon bottles. Dilutions of samples were made with high-purity water obtained by sub-boiling distillation of deionized feedwater using a conditioned quartz still. Reagent grade nitric acid (Baker Analyzed, J.T. Baker, Phillipsburg, NJ) and high-purity deionized water from an in-house purification plant were used for cleaning all materials and containers. The reductant solution, 10% (w/w) SnCl<sub>2</sub> in 7% (w/w) HCl, was prepared from tin(II) chloride dihydrate (Baker Analyzed) and hydrochloric acid (Baker Intra-Analyzed), which were obtained from J.T. Baker. The solution was agitated prior to use to remove any residual mercury contamination. Potassium dichromate (AR grade) was obtained from Mallinckrodt (Paris, KY).

**Isotopic Spike and Calibration Materials.** The <sup>201</sup>Hg-enriched spike material (95.5% atom fraction <sup>201</sup>Hg, 2.8% atom fraction <sup>202</sup>Hg, atomic weight 200.982) was purchased from Oak Ridge National Laboratory (Oak Ridge, TN) as solid mercuric oxide. The isotopic composition of the spike material provided on the certificate was verified by ICPMS measurement. A stock solution of the spike (100 ng/g) was prepared by dissolution in high-purity nitric acid and serial dilution with a preservative solution containing 0.05% (w/v) potassium dichromate in 3% (v/v) nitric acid. The stock solution was stable for at least three months when stored in a refrigerator at 4 °C. The spike was calibrated for each use by reverse isotope dilution using serially diluted SRM 3133, Mercury Standard Solution (Standard Reference Materials Program, NIST, Gaithersburg, MD).

**Digestion Apparatus.** Digestion tubes, comprising a modified Carius design, were similar to those used previously at NIST for the measurement of sulfur.<sup>36,37</sup> The tubes (25.4 cm long) were fabricated in-house from thick-wall (3 mm) borosilicate glass tubing. The tubes were annealed at 560 °C and then cleaned prior to use by partially filling with high-purity nitric acid followed by refluxing overnight on a hot plate. Sealed tubes were placed inside heavy steel shells (37 cm long), each having a threaded end cap and a sealing gasket consisting of a 32 mm × 1.5 mm copper disk. A cross-sectional diagram of the Carius tube and shell assembly is shown in Figure 1.

**Coal Reference Materials.** Coal reference materials used in this study were SRM 1632b, 1632c, and 1633b; BCR 40 (Steam Coal), 180 (Gas Coal), and 181 (Coking Coal); and SARM 20, a Sasolburg sub-bituminous to bituminous coal.

**Sample Processing.** Approximately 0.25–0.3 g of undried coal was weighed by difference into a Carius tube using a borosilicate glass boat-shaped transfer funnel. The end of the funnel could be inserted vertically into the neck of the Carius tube to facilitate transfer with no extraneous loss of material. The coals were then spiked with a weighed aliquot of <sup>201</sup>Hg-enriched stock

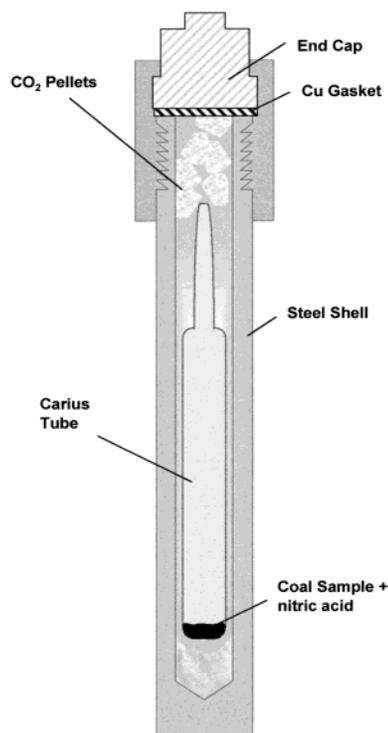


Figure 1. Cross section of Carius tube/steel sleeve assembly.

solution via a plastic syringe. The amount of spike added was designed to yield a <sup>201</sup>Hg/<sup>202</sup>Hg isotope ratio in the range 2–3. This represented a compromise between minimizing the error propagation factor and minimizing analytical measurement precision, background contribution effects on <sup>202</sup>Hg, and detector dead-time errors on the <sup>201</sup>Hg. Six grams of nitric acid was added to each Carius tube, and the contents were frozen by placing the tube in a beaker containing a slush mixture of solid CO<sub>2</sub>/CHCl<sub>3</sub>/CCl<sub>4</sub>. The neck of the tube was then sealed using a methane/oxygen gas torch. The sealed tubes were inserted into steel shells, along with 20 g of solid CO<sub>2</sub> pellets, to maintain equal pressure across the tube wall when heated, and placed inside a laboratory oven at 240 °C for ~12 h. This treatment completely combusts the organic matrix, converting all carbon to CO<sub>2</sub>. After cooling to room temperature, the Carius tubes were vented and the contents transferred to 50-mL high-density polypropylene centrifuge tubes and diluted with quartz-distilled water to yield a mercury concentration not exceeding 0.5 ng/g. This concentration represented the upper limit of linearity of the instrument; therefore, the working concentration was always lower than this. The tubes were lightly capped and allowed to stand in a refrigerator overnight to degas excess CO<sub>2</sub> and NO<sub>2</sub> resulting from the combustion process. The solutions were then analyzed by cold-vapor generation ICPMS without further treatment.

Separate 1-g subsamples of the coals were dried under dry high-purity nitrogen gas for 1 h at 107 °C to provide moisture correction factors which were used to correct the analytical data to a dry weight basis.

**Safety Considerations.** Carius tube combustion involves the generation of internal pressures in excess of 1 × 10<sup>7</sup> Pa (100 atm) at 240 °C. Extreme care should be used in the handling and venting of pressurized tubes. Tubes having any defects or small holes should not be used as they represent a severe explosion

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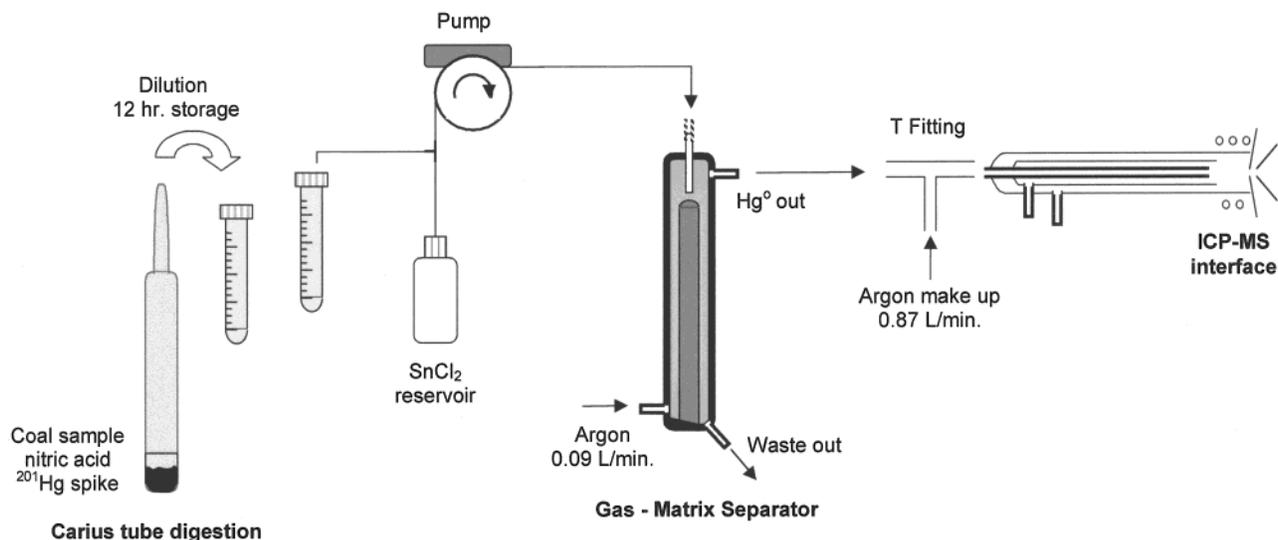


Figure 2. Schematic of cold-vapor generation ICPMS measurement process.

hazard from pressurized CO<sub>2</sub>. The venting process should be conducted behind an appropriate explosion-resistant safety shield by appropriately trained personnel. A discussion of Carius tube design for minimizing losses and hazards by explosion has been provided by Gordon.<sup>38</sup>

**Instrumentation and Isotope Ratio Measurements.** Mercury in the combusted samples was converted to atomic vapor by mixing with the tin chloride reductant solution via a four-channel peristaltic pump (Gilson, Villiers Le Bel, France) and pumping through a commercial gas-matrix separator (CETAC Technologies, Omaha, NE). Separated mercury vapor was introduced directly into the torch injector of a VG PQ2 quadrupole instrument (VG Elemental, Winsford, Cheshire, U.K.) using an argon carrier stream via a transfer line of 1.6-mm-i.d. Viton tubing. A makeup argon gas stream, intended to maintain the correct overall injector gas flow to the torch, was mixed with the gas stream exiting the gas-matrix separator using a small polypropylene Tee piece. Mercury contamination was removed from the argon supply gas by passing through a tube containing a gold mesh. This was periodically heated to remove any trapped mercury. A schematic of the complete experimental process is shown in Figure 2. <sup>201</sup>Hg/<sup>202</sup>Hg isotope ratios were measured using a time-resolved acquisition (TRA) mode with a dwell time of 80 ms per isotope. A TRA mode was used because it facilitated dynamic instrument background subtraction of the measurement isotopes. The resulting data matrix was downloaded to a computer spreadsheet program from which background-corrected <sup>201</sup>Hg/<sup>202</sup>Hg ratios were calculated. This has been described in detail by Christopher et al.<sup>35</sup> The experimental measurement parameters are summarized in Table 1. Correction of the analytical data for instrument mass discrimination was not necessary, as the instrumentation used did not exhibit any mass discrimination at high masses. This was confirmed by measuring <sup>201</sup>Hg/<sup>202</sup>Hg ratios on a diluted aliquot of SRM 3133 (Mercury Standard Solution). These were identical to IUPAC tabulated values within the measurement uncertainty. The data were, however, corrected for detector system dead-time effects. The instrument dead time was measured using SRM 3133 and was found to be 35 ns.

Table 1. Cold-Vapor ICPMS Measurement Parameters

Gas-Matrix Separator	
carrier gas flow rate	0.09 L/min
SnCl <sub>2</sub> flow rate	1.5 mL/min
sample uptake flow rate	3.5 mL/min
ICPMS	
plasma gas flow rate	14.2 L/min
auxiliary gas flow rate	0.60 L/min
injector makeup gas flow rate	0.87 L/min
total injector flow rate	0.96 L/min
forward rf power	1.35 kW
peak jumping points per peak	1
dwell time per peak	80 ms
total acquisition time	60 s
multiplier dead time correction	80 ns

Spectral interferences from other polyatomic ions are generally not present when the <sup>201</sup>Hg and <sup>202</sup>Hg isotopes are measured, as these masses are relatively high. Measurements on unspiked coal materials did not show any evidence of spectral interferences at these masses or indeed any other ions with the exception of tin from the reduction process. This illustrates the effectiveness of the separator cell in removing mercury from the rest of the sample matrix.

## RESULTS AND DISCUSSION

**Procedural Blank and Detection Limit.** An assessment of the blank contribution was made by adding a very small amount (1 ng) of the <sup>201</sup>Hg spike to a Carius tube, adding nitric acid, and processing through the entire analytical procedure. The average absolute blank contribution was 30 pg (1σ = 14.4 pg) for a set of 17 separate measurements over a three-month period. The blank contribution was a factor of ~10 lower than an equivalent sample preparation scheme using microwave digestion with nitric and perchloric acids. The extremely low blank for this method is attributed to the high temperatures involved during the fabrication of the Carius tubes, which effectively removes any mercury contamination, combined with the ability to use nitric acid alone as an oxidant. The simplicity of the sample preparation scheme and the use of a completely closed system, which eliminates any

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Table 2. Method Recovery for Mercury Standard Solution (SRM 3133) Using the Carius Tube Digestion Process and Determined by CV-ID-ICPMS

recovery experiment	total Hg (ng)		recovery (%)
	added	measured	
SRM 3133 aliquot 1	19.914	19.942	100.14
SRM 3133 aliquot 2	21.905	21.950	100.21

risk of external contamination, also contribute to the low blank levels. Tests conducted on the vessels and containers indicated that most of the blank contribution was from the nitric acid. Further purification of the acid should yield even lower blanks. Nevertheless, for the samples measured in this study, the blank levels were so low that they represented a negligible uncertainty contribution.

The sensitivity enhancement for mercury relative to the traditional approach of solution sample introduction was found to be considerable. The instrument detection limit for cold-vapor generation was 0.5 pg/mL ( $3\sigma$ ,  $n = 10$ ). This was  $\sim 300$  times lower than the instrument detection limit using solution sample introduction. The improved sensitivity is attributable to the improvement in efficiency of transferring mercury from the sample to the plasma source and also because the ionization processes take place under "dry" plasma conditions. It is clear, however, when the instrument detection limit capabilities are compared with the method blank that the method is essentially blank limited. Thus, a practical detection limit in coal, based on a per batch variability of the process blank, is  $\sim 40$  pg/g ( $3\sigma$ ).

**Analytical Precision and Performance.** The analytical measurement reproducibility was assessed by taking 10 replicate isotope ratio measurement sets on each of two different coal digestates and calculating the relative standard deviation of the calculated concentrations. This approach eliminates any variability due to inhomogeneity of the coal material. In both cases, the analytical measurement reproducibility was 0.5% relative. The measurement reproducibility, as well as sensitivity, may be further improved by optimization of the instrument dwell time and adjustment of both the gas and liquid flow rates through the gas-matrix separator. A systematic study of these parameters, which require some hardware and software configuration changes, is being conducted in our laboratory.

One of the advantages of isotope dilution is that complete recovery of the analyte is not necessary once chemical equilibration of the spike has been achieved. The closed environment of

the Carius digestion process ensures that no mercury losses by volatilization can occur before equilibration takes place. An assessment of method accuracy was performed in duplicate by adding an accurately known amount ( $\sim 20$  ng) of a mercury primary standard (SRM 3133) to a Carius tube, spiking with  $^{201}\text{Hg}$ , and processing through the entire analytical procedure. The measured "recoveries" of the primary standard are listed in Table 2. The amounts determined differ from the true amounts by 0.1–0.2% relative, which is well within the 0.5% relative precision of the method.

Although the Carius combustion process for coal requires  $\sim 12$  h, it is readily amenable to batching, such that a large number of samples may be processed at one time. The analytical measurement is extremely rapid, and  $\sim 10$  samples can be analyzed in 1 h. The sample throughput of the method is therefore considered to be very good. Memory effects associated with instrument washout were found to be much lower than with solution nebulization, as the absolute amount of mercury introduced into the sample introduction system is much lower and the exposed surface area of the glassware is also much lower than a typical solution introduction setup. For these reasons, it was possible to reduce the mercury background within 60 s of washout, from  $\sim 500\,000$  counts/s to below 1000 counts/s using a 10% (w/v) solution of nitric acid or below 500 counts/s using a 1% (w/v) solution of cysteine.

**Mercury Determinations in SRM 1632b, 1632c, and 1633b.** The method was first applied to the determination of mercury in SRM 1632b and a renewal material, SRM 1632c, both of which are bituminous coals from the Pittsburgh coal seam, USA. Analytical data for these materials are summarized in Table 3. SRM 1632b was used as a control in both phase 1 and phase 2 of the CONSOL study.<sup>32</sup> The analytical data generated from each of these two phases are shown for comparison in Figure 3, together with the data from this present work. Each of the points from the CONSOL study represents data from a single laboratory together with the mean calculated across all the laboratories. The vertical error bars on the mean values represent the 95% confidence interval on the data. Data for the present work are individual measurements from six separate bottles of SRM 1632b. The mean value (solid line) and the 95% confidence interval (dashed lines) are shown in Figure 3. For comparison purposes,  $\pm 10\%$  reference intervals about the mean value are also plotted. Clearly the difference between the means from the two phases of the CONSOL study approaches 20%, although the value obtained by averaging the means from the two phases (0.077 mg/kg) coincides

Table 3. ID-CV-ICPMS Mercury Data for NIST SRM 1632b (Coal), 1632c (Coal), and 1633b (Coal Fly Ash)

coal	classification	no. of replicates	moisture correction <sup>d</sup> (%)	ID-CV-ICPMS				
				Hg concn <sup>b</sup> (mg/kg)	standard deviation (mg/kg)	expanded uncertainty <sup>c</sup> (mg/kg)	other values (mg/kg)	uncertainty (mg/kg)
SRM 1632b	bituminous	6	1.54	0.0774	0.0021	0.0022	0.07 <sup>d</sup>	
SRM 1632c	bituminous	6	1.51	0.0943	0.0009	0.0013	0.0933 <sup>e</sup>	0.0032
SRM 1633b	bituminous fly ash	7	0.32	0.1431	0.0015	0.0018	0.141 <sup>f</sup>	0.019

<sup>a</sup> Correction based on drying of separate sample at NIST under dry high-purity nitrogen gas for 1 h at 107 °C. <sup>b</sup> Dry weight mercury concentration based on arithmetic mean of  $n$  determinations. <sup>c</sup> Calculated expanded uncertainty for a 95% confidence interval. <sup>d</sup> NIST Information value by CVAAS. <sup>e</sup> NIST RNAA data. The RNAA and ID-CV-ICPMS data have been combined to produce a NIST certificate value for SRM 1632c. <sup>f</sup> NIST certified value by CVAAS.

Table 4. ID-CV-ICPMS Mercury Data for BCR Coals 40, 180, and 181 and SARM Coal 20

coal	classification	no. of replicates	moisture correction <sup>a</sup> (%)	ID-CV-ICPMS			certified values <sup>d</sup> (mg/kg)	stated uncertainty <sup>e</sup> (mg/kg)
				Hg concn <sup>b</sup> (mg/kg)	standard deviation (mg/kg)	expanded uncertainty <sup>c</sup> (mg/kg)		
BCR 040	steam coal	6	1.40	0.4332	0.0088	0.0097	0.35	0.06
BCR 180	gas coal	3	1.51	0.1250	0.0025	0.0038	0.123	0.008
BCR 181	coking coal	3	1.21	0.1358	0.0042	0.0062	0.138	0.011
SARM 20	bituminous	6	6.49	0.2526	0.0033	0.0040	0.250	-0.07 +0.02 <sup>f</sup>

<sup>a</sup> Correction based on drying of separate sample at NIST under dry high-purity nitrogen gas for 1 h at 107 °C. <sup>b</sup> Dry weight mercury concentration based on arithmetic mean of *n* determinations. <sup>c</sup> Calculated expanded uncertainty for a 95% confidence interval. <sup>d</sup> The arithmetic mean of the mean data values from *n* participating laboratories, where *n* is 10 for BCR 40 and 11 for BCR 181 and 182. <sup>e</sup> 95% confidence interval. <sup>f</sup> Asymmetric uncertainty limits.

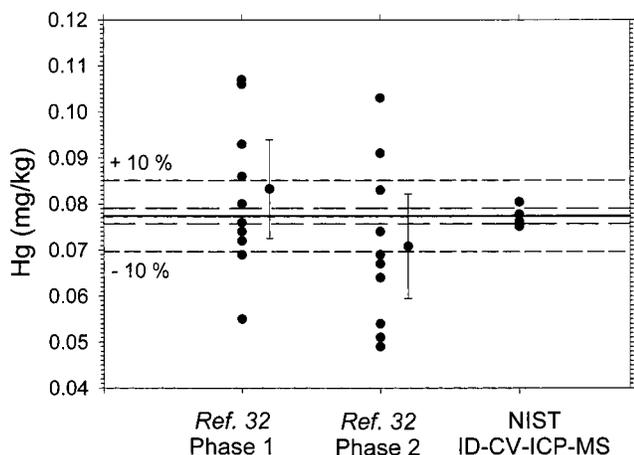


Figure 3. Analytical performance data for mercury in NIST SRM 1632b. Comparison of data abstracted from ref 32 and from the present method. The thick solid line is the mean value obtained by ID-CV-ICPMS; the long dashed lines represent the 95% confidence interval. Short dashed lines are  $\pm 10\%$  reference intervals for comparison.

with the value from the present study. The small spread of the data generated from this method indicates that SRM 1632b is fairly homogeneous for mercury.

Several measurements were also made on SRM 1633b, which is a bituminous coal fly ash. This material was originally certified using CVAAS, but the uncertainty was relatively large ( $\pm 13\%$ ). This could be attributed to either poor reproducibility of the analytical method or inhomogeneity of the material. The mercury data measured in this work for SRM 1633b are summarized in Table 3, indicating that the original certified value is relatively accurate but that the large expanded uncertainty is a consequence of poor analytical performance of the method. Based on the present data, the homogeneity of SRM 1633b appears to be equal to or better than 1%.

As an additional check on the performance of the analytical method, a series of measurements were made on SRM 1633b, in which three individual sample aliquots of increasing size were weighed into Carius tubes and processed through the method. In each case, the absolute amount of mercury determined was plotted against the corresponding sample aliquot weight. As should be expected from a system in analytical control, the plot showed a strong linear regression, with an  $r^2$  value of 0.999 98. The slope of the plot represents the concentration of the mercury in the material, which was calculated to be 0.1414 mg/kg. This

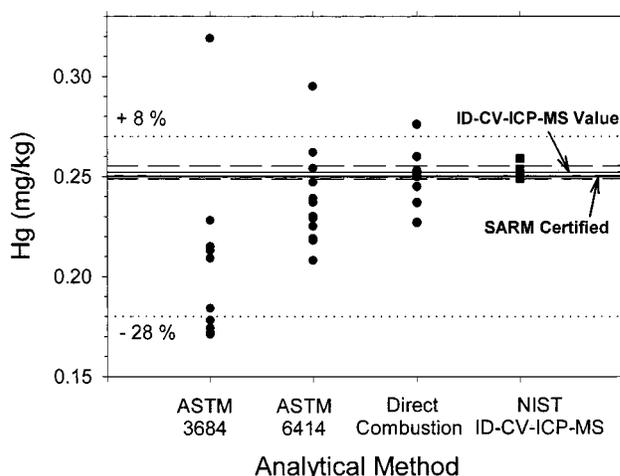


Figure 4. Analytical performance data for mercury in SBS SARM 20. Comparison of data abstracted from ref 33 and from the present method. The thick solid line is the SARM certified value; the thin line is the value obtained by ID-CV-ICPMS. Dotted lines are the SARM uncertainty limits; dashed lines are the expanded uncertainty limits (95% CI) by ID-CV-ICPMS.

compares very well with the mean value of 0.1431 measured for the seven replicates (Table 3).

**Mercury Determinations in BCR 40, 180, and 181 and SARM 20.** Mercury measurements were also made on BCR materials 40, 180, and 181 using the new method. These data are summarized in Table 4. The concentrations for BCR 180 and 181 agreed well with the values listed on the certificates; however, the concentration measured for BCR 40 was  $\sim 24\%$  higher than the certificate value. The 95% confidence interval calculated from the multilaboratory data for this material is  $\sim 18\%$ , but this does not overlap with the mean and confidence interval using the ID-CV-ICPMS method, so there appears to be a negative bias in the certified value. It should be noted, however, that BCR 40 was certified in 1984 and is now out of stock.

In contrast, there was good agreement between the data generated from SARM 20 (Table 4) and the certified value. SARM 20 was included in phase 2 of the multilaboratory study organized by EPRI.<sup>33</sup> These data are summarized in Figure 4. Over 85% of the participating laboratories used either ASTM method D3684 (bomb combustion CVAAS), ASTM D6414 (acid extraction CVAAS or CVAAS), or an ASTM direct combustion method. As is noted in the report, the bomb combustion method is biased low, which is attributable to the ash content, resulting in poor combustion.

The certified value for SARM 20 (0.25 mg/kg) is shown as a thick solid line in Figure 4. The value obtained in the present work is shown as a thin solid line, with the expanded uncertainty (95% confidence interval) as dashed lines. The expanded uncertainty was calculated by combining type A and type B uncertainty components according to ISO guidelines.<sup>39</sup> In contrast, the uncertainty limits on the certified value are asymmetric and relatively large at +8% and -28% of the certified value, reflecting the range of data used in the certification process.<sup>40</sup> This ranged from a mean of 0.175 mg/kg for the lowest laboratory to 0.303 mg/kg for the highest laboratory, with 0.250 mg/kg as the median value. The small uncertainty of our data set demonstrates that the coal is very homogeneous and that the uncertainty limits on the certified value are directly related to method performance of the participating laboratories.

## CONCLUSIONS

A method employing closed-system combustion and cold-vapor generation combined with isotope dilution mass spectrometry has been successfully developed and has been applied to the determination of mercury in three NIST SRMs and four international coal reference standards. The combustion step facilitates complete destruction of the matrix, complete conversion of all species of mercury to Hg<sup>2+</sup>, and complete chemical equilibration with the added spike. The closed environment of the Carius tube also ensures that no external contamination of the sample or loss of mercury is possible. Any subsequent loss of mercury, for example, to container walls or losses during sample manipulation, does not affect the accuracy of the method once equilibration of analyte and isotopic spike has been achieved. All data thus far indicate that the nitric acid used for the digestion is the predominant source of the blank. It was possible to perform these determinations in a routine laboratory environment because of the short time of exposure of the sample to the laboratory atmosphere and the extremely small cross-sectional area of the Carius tube opening.

(39) *Guide to the Expression of Uncertainty in Measurement*, 1st ed.; ISO: Geneva, Switzerland, 1993.

(40) *The Preparation of Three South African Coals for Use as Reference Materials*; Report No. M169; MINTEK, Randburg, 2125 South Africa, 1984.

The relative reproducibility of the method is ~0.5% at the 0.1 mg/kg level (100 ng/g), which is a fairly typical concentration for mercury in coal. The availability of a primary method of demonstrated accuracy and reproducibility will permit the certification of mercury in a series of NIST coal SRMs with much better estimates of the true values and with much lower uncertainties than previously achievable. This will provide an improved traceability link with which to evaluate other analytical methods and instrumentation calibrations. The use of cold-vapor mercury generation is a considerable advantage in that it affords complete separation of mercury from the rest of the sample matrix and much higher sensitivity than conventional sample introduction processes. The method should, therefore, allow accurate determinations of mercury at extremely low concentrations in coal.

The method is equally applicable to all other types of matrix that are amenable to Carius tube digestion and can readily be adapted to the measurement of mercury in soils, sediments, crude oil, and other petroleum products. There is limited analytical data for petroleum products at the present time because of the low levels of mercury present and the complexity of the matrix. The high sensitivity of this method should be ideal for making accurate measurements on these products. This sensitivity, combined with the ability to separate mercury from the rest of the sample matrix by cold-vapor generation, should also prove useful in environmental tracer studies, where the amount of tracer that can be added to the system is often limited.

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